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13. ABSTRACT *(Maximum 200 words)*

We have investigated the growth of (Zn,Mn)(S,Se) epitaxial layers of high structural quality on (100) GaAs substrates. Double crystal x-ray diffraction (DCXRD) measurements indicate that quaternary epilayers nearly lattice-matched with GaAs are characterized by DCXRD curves with a full width at half maximum in the range 30 - 60 arc seconds. This indicates the successful fabrication of epitaxial layers with excellent structural integrity. Photoluminescence (PL) spectroscopy is employed to map the variation of the energy gap of the quartenary alloys over a wide range of alloy compositions. It is found that exchange related effects on band gap bowing lead to a smaller than anticipated increase in the energy gap as a function of the Mn composition. Finally, temperature dependent PL is used to examine the viability of (Zn,Mn)(S,Se) alloys as confining layers for ZnSe and (Zn,Cd)Se quantum wells. Efficient exciton confinement is demonstrated through the observation of robust PL from such quantum wells up to high temperatures. However, the renormalization of the quartenary band gap by spin fluctuations leads to a rapid decrease in the energy gap of the (Zn,Mn)(S,Se) alloys with increase in temperature, leading to limitations in quantum confinement, particularly in the conduction band.

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Fabrication and Characterization of New Quantum Structures for Blue Lasers

Final Technical Report

Professor N. Samarth

Grant DAAH04-94-G-0394

The Pennsylvania State University

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A. STATEMENT OF PROBLEM STUDIED

The proposed work in the original project was to explore new wide-gap II-VI heterostructures for light emitters that function at short visible wavelengths. The intent was to examine the growth and structural/optical properties of heterostructures derived from the wide bandgap II-VI magnetic semiconductor (MS) alloys, specifically the quartenary system (Zn,Mn)(S,Se). Apart from applications in the short wavelength region of the visible spectrum, such heterostructures have received substantial attention for several years because of the fundamentally interesting magneto-optical phenomena (e.g. spin superlattice formation and a giant quantum confined Faraday effect) that result from the exchange interaction between electrons in extended band states and in localized 3d states [1-4]. A parallel outcome of the growth of such heterostructures is that they extend the possibilities of lattice constants and bandgaps available within the context of opto-electronic applications of II-VI heterostructures at short visible wavelengths [5]. For instance, the (Zn,Mn)(S,Se) alloy system [6-9] offers an interesting alternative to the better investigated (Zn,Mg)(S,Se) buffer layers [5] currently used to confine the optically active region of these devices. Like Mg, the addition of Mn into a II-VI semiconductor such as ZnSe opens up the bandgap and increases the lattice constant. However, the presence of Mn also introduces additional effects such as an absorption band in the vicinity of 2.3 eV as well as a renormalization of the bandgap by spin fluctuations.

While such phenomena raise interesting fundamental questions, their influence on device applications of MS alloys needs to be carefully considered. This report discusses our research into the (Zn,Mn)(S,Se) material system and related heterostructures. We first discuss our efforts to lattice-match (Zn,Mn)(S,Se) to GaAs substrates in an effort to produce buffer layers of higher structural integrity than than the ZnSe buffer layers typically employed for MS quantum structures. The successful achievement of this goal is important for the fabrication of high quality MS heterostructures for sophisticated magneto-optical studies. Next, we discuss the growth and optical characterization of larger regions of the quaternary phase diagram and explore the potential of this material to act as a confining layer for II-VI quantum wells (Qws). This work is in press in the proceedings of the Fall 1996 MRS Meeting and is also being prepared as a rapid publication. It also constitutes a substantial portion of a PhD dissertation.

Finally, it is important to mention that the graduate student being trained under this project also contributed to related collaborative projects involving the characterization of ZnSe-based epilayers and heterostructures using ellipsometry and electron energy loss spectroscopy. While these techniques have not yet been applied to the quartenary system of interest in this project, the measurements were applied to the ZnSe and (Zn,Cd)Se systems, hence building up a database of dielectric functions and surface characterization data of crucial importance for future studies of the quartenary alloy. This work resulted in high-profile, rapid publications in Surface Science Letters and Applied Physics Letters. The support of this ARO grant was also acknowledged for these publications since the work would not have been possible otherwise.

B. SUMMARY OF THE MOST IMPORTANT RESULTS

Sample growth was carried out on (100) GaAs substrates in a cryoshrouded MBE chamber using Zn, Mn, Se, and ZnS sources of 6N, 5N, 5N and 5N purity, respectively, evaporated from standard effusion cells. *In situ* reflective high energy electron diffraction (RHEED) at 12 keV monitored the surface during growth. Background pressures in the chamber during growth are typically $\sim 10^{-10}$ torr. Growth rates of the various materials grown were measured using RHEED intensity oscillations and sample compositions of calibration epilayers determined by electron probe microscopy. Structural characterization was carried out using double-crystal x-ray diffraction measurements. The steady state photoluminescence (PL) of these samples was measured using lock-in techniques in a 0.4 m spectrometer equipped with a cooled PMT over the temperature range 4K - 300K in a continuous flow optical cryostat using the 325 nm line of a HeCd laser with an incident intensity of about 1 W/cm^2. The temperature of the sample during PL measurements was measured using a Rh-Fe thrmocouple heat sunk to the sample stage.

We first discuss the growth and characterization of $Zn_{1-x}Mn_xS_ySe_{1-y}$ epilayers of 1-4 microns thickness in the composition range $0<x<0.09$, $0<y<0.36$. Substrate temperatures during growth are typically in the range 150-300° C. Due to the relatively high vapor pressure, significant incorporation of sulfur does not occur unless the substrate temperature is lower than ~250° C. This lowering of substrate temperature necessitates careful adjustment of other growth parameters to obtain high quality layers. A rough idea of layer quality is obtained by observing the RHEED pattern which is typically streaky and unreconstructed. An increased roughening of the surface is observed with increasing sulfur content. We speculate that the rough surface growth stems from the decreased surface mobility of the adatoms at these lower growth temperatures.

Figure 1 shows DCXRD scans from two of the quartenary epilayers. The relative position of the diffraction peak with respect to that from GaAs shows that these epilayers have ~ 0.05% lattice mismatch with the substrate. Due to the fact that this mismatch is much smaller than that of ZnSe on GaAs, we find a significant improvement in the structural quality of the epilayers, with half widths in the range of 35 - 65 arcseconds. For comparison, the typical widths of rocking curves reported by most researchers for ZnSe epilayers of similar thickness grown on (100) GaAs lies in the range 150 - 200 arcseconds. More recently, significant improvements in the structural quality of ZnSe epilayers has been reported in work that has paid careful attention to the inital nucleation of ZnSe growth on GaAs, resulting in DCXRD widths of ~ 27 arc seconds [10].

The low temperature energy gaps of the quartenary alloys are estimated from the near band-edge PL and range from near that of ZnSe (2.8 eV) to as high as 3.1 eV. A summary of the variation of the band gap with alloy composition is shown in Fig. 2. We note that

these estimates are probably lower than the actual band gap since it is likely that the PL from the quartenary alloy epilayers originates from the recombination of excitons localized in a disorder induced tail to the density of states. Judging from the widths of the PL spectra, Stokes' shifts of up to 30 meV are likely to be encountered.

Naively, one might anticipate that the energy gap variation with the quartenary alloy composition may be estimated from the energy gaps of the binary end points: ZnSe (2.8 eV), MnSe (~3.2 eV), ZnS (3.8 eV) and MnS (~3.7 eV). However, as can be seen in the figure above, the energy gap of the quartenary alloy does not vary much with Mn concentration in the composition range studied here. This is rooted in the same physics that leads to the unusual nonmonotonic relationship between x and E_g in $Zn_{1-x}Mn_xSe$ alloys which show a small minimum for low x [11]. This "bowing" of the energy gap in MS alloys arises because of the strong *sp-d* exchange interaction between conduction and valence band states and the localized 3d Mn states. When the *s-pd* exchange is included as a perturbation in the standard crystal Hamiltonan, the band gap has second-order corrections that involve the averages of two-spin correlation functions.

These corrections can be reformulated in terms of the magnetic susceptibility and essentially result in an energy gap which varies with concentration x and temperature T as [11]:

$$E_g\ (x) = E_o\ (T)\ + ax - b\chi(x)T\ ,$$

where a and b can be treated as empirical fitting parameters, χ is the magnetic susceptibility, and T is temperature and $E_0\ (T)$ describes the temperature variation of the band-gap due to non-magnetic effects (the Varshni dependence [12]). The magnetic susceptibility has a Curie-Weiss form and is a nonlinear function of concentration, exhibiting a maximum at a Mn concentration $x \sim 0.1$ due to the anti-ferromagnetic coupling between the Mn spins. At very low values of x, a large number of Mn spins are isolated and the susceptibility increases with x. As the concentration increases, the Mn spins begin to compensate for one another, negating their contribution to the susceptibility. Therefore, the negative term is largest at small x, resulting in very little variation of E_g with x. For this reason, the Mn concentration has a minimal contribution to the band gap for the composition range examined in this study. Further, the spin-dependent contribution to the band gap strongly affects the temperature variation of E_g.. An important feature of this unusual variation of bandgap with temperature is that the energy gap of a MS alloy decreases with temperature more rapidly than the non-magnetic II-VI host lattice.

The realization that the energy gap of (Zn,Mn)(S,Se) alloys red shifts with increasing temperature at a faster rate than that of ZnSe or Zn(S,Se) raises a cautionary note about the use of this material for short wavelength applications. In order to examine the

efficiency of (Zn,Mn)(S,Se) epilayers as confining barriers, we have embedded quantum wells of ZnSe and (Zn,Cd)Se within the epitaxial quartenary layers. Fig. 3 shows a typical PL spectrum from a sample containing two isolated, single QWs of 5 nm ZnSe and 6.5 nm (Zn,Cd)Se. We estimate the conduction (valence) band offsets to be roughly 20 meV (100 meV) and 150 meV (150 meV) for the ZnSe QW and the (Zn,Cd)Se QW, respectively. The spectrum shows 4 distinct features:

(a) A broad, orange ($E_{PL} \sim 2.1$ eV) emission from the Mn^{2+} intraionic $^4T_1 \rightarrow {}^6A_1$ transitions.
(b) A strong emission in the vicinity of 2.6 eV from the (Zn,Cd)Se QW;
(c) A strong emission in the vicinity of 2.8 eV from the ZnSe QW;
(d) A weak near band edge PL from the quaternary epilayer at 2.9 eV

The strong PL from the QWs remains quite efficient up to room temperature but also shows a significant inhomogeneous broadening of ~20 meV and ~ 40 meV for the ZnSe and (Zn,Cd)Se QWs, respectively. This should be compared to the typical 5-10 meV PL linewidths obtained for similar QWs in a ZnSe host lattice. The presence of low-energy tails in the PL spectra are indicative of exciton localization in fluctuations of the confining potential due to interdiffusion at the well interfaces.

Variation in PL spectra with temperature provides additional information about these structures. Studies have been performed on several samples at temperatures up to 300K. In order for this material to be useful as a confining region for optoelectronic applications, it must continue to act as a barrier to the optically active region at high temperatures. As shown in Figure 4, the increased rate of bandgap closure with temperature due to the *sp-d* exchange interactions results in a barrier band gap that decreases with temperature more rapidly than that of the quantum well material. The consequent decrease in quantum confinement creates a rapid redshift of the luminescence and increased thermalization of the well excitons. Despite the reduced confinement, the PL from these samples is quite strong, even up to room temperature. The PL from the shallower ZnSe quantum wells, however, does tend to vanish at higher temperatures (~200K) as the excitons are thermalized from the well. At room temperature, the remaining signal is from the barrier and the deeper (Zn,Cd)Se quantum well, showing that as long as the barrier is high enough, (Zn,Mn)(S,Se) performs quite effectively as a confining material

C. LIST OF PUBLICATIONS AND TECHNICAL REPORTS

1. F. Flack, N. Samarth and F. Semendy, "Growth and Characterization of $Zn_{1-x}Mn_xSe_{1-y}S_y$ Epilayers and Related Heterostructures," in <u>Advances in Microcrystalline and Nanocrystalline Semiconductors: Symposium Q</u>, edited by P. Alivasatos, R. Collins and P. Fauchet, (Materials Research Society Symposium Proceedings, in press, Pittsburgh, 1997).

2. J. Lee, R.W. Collins, A. R. Heyd, F. Flack, and N. Samarth, "Spectroellipsometric characterization of Zn(1-x)Cd(x)Se multilayered structures on GaAs," Appl. Phys. Lett. 69, 2273 - 2775 (1996)
3. J. Lee, Byungyou Hong, J.S. Burnham, R.W. Collins, F. Flack, and N. Samarth."Spectroellipsometry studies of Zn(1-x)Cd(x)Se: From Optical Functions to Heterostructure Characterization" in Diagnostic Techniques for Semiconductor Materials Processing, edited by S.W. Pang, O. J. Glembocki, F. H. Pollack, F. Celii, and C. M. Sottomayor-Torres, (Materials Research Society Symposium Proceedings, Vol. 406, Pittsburgh, 1996).
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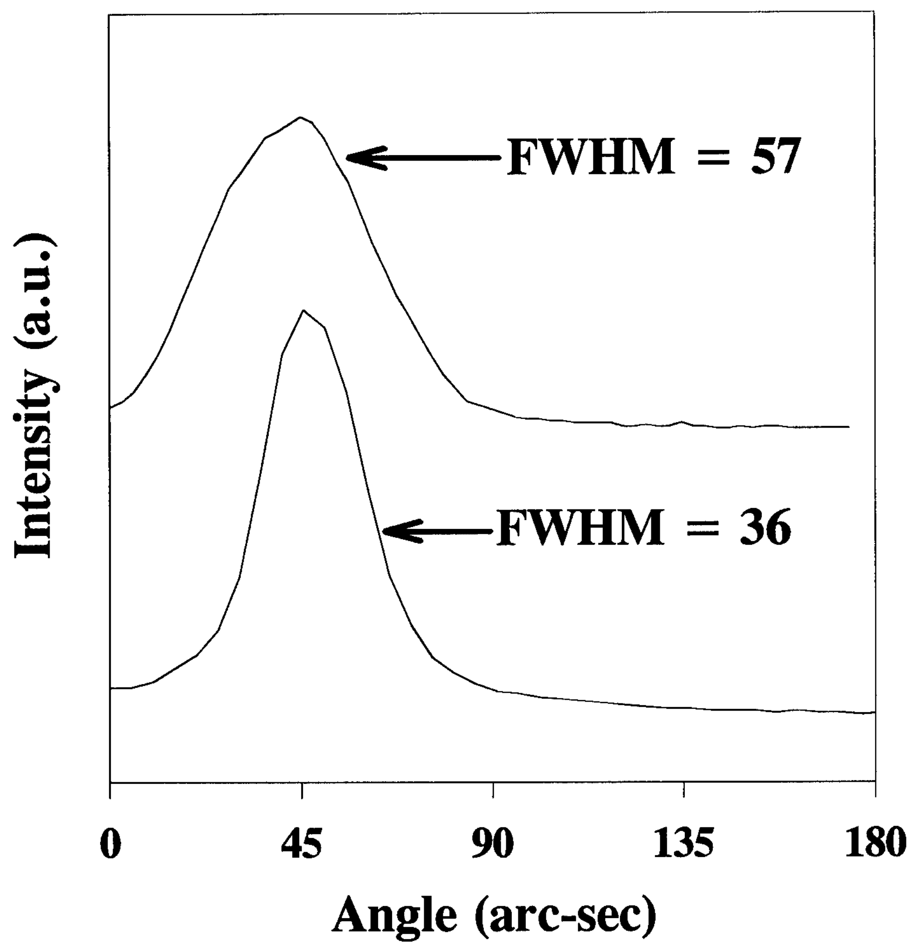

Fig. 1. DCXRD measurements for two (Zn,Mn)(S,Se) epilayers. The compositions of the two samples are: $Zn_{0.89}Mn_{0.11}S_{0.13}Se_{0.87}$ (upper curve) and $Zn_{0.93}Mn_{0.07}S_{0.11}Se_{0.89}$ (lower curve).

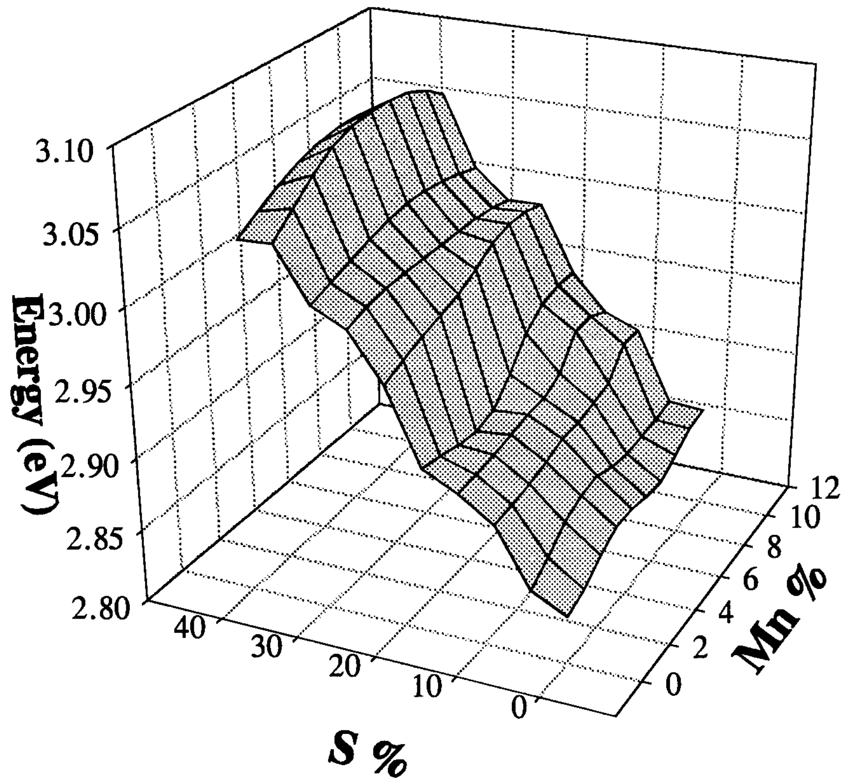

Fig. 2. Variation in band gap with both sulfur and manganese content for the samples studied. The energy gap vs. composition surface is produced by estimating the band gap from PL studies of 21 samples of (Zn,Mn)(S,Se) of different compositions. Note that the variation of the band gap with sulfur content qualitatively follows standard expectations for a semiconductor alloy while there is little change in the band gap with manganese content.

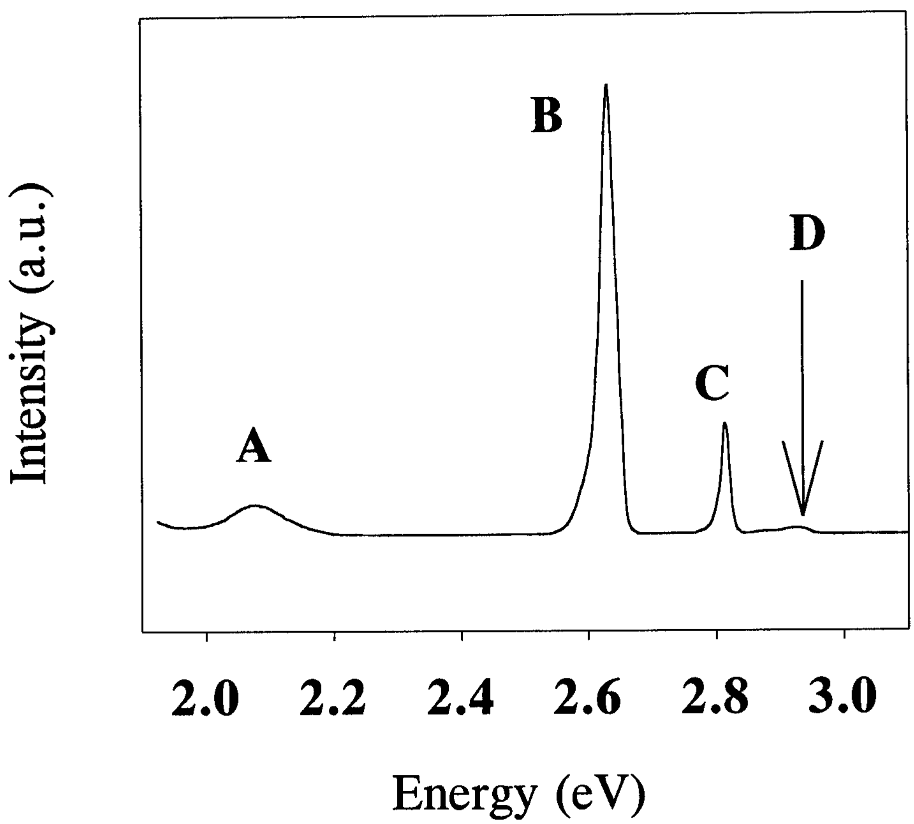

Fig 3. PL emission spectrum at 4 K taken from a $Zn_{0.82}Mn_{0.18}S_{0.20}Se_{0.80}$ epilayer containing a 50 Å ZnSe QW and a 65Å $Zn_{0.75}Cd_{0.25}Se$ QW.

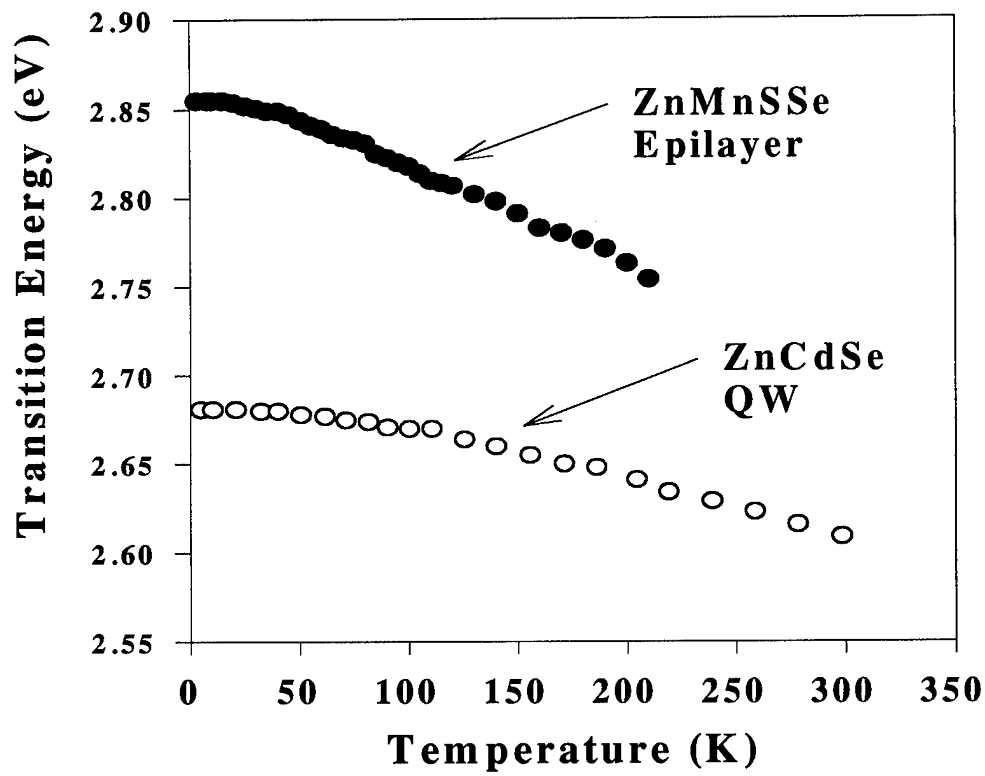

Fig 4. Temperature dependence of the energy position of the PL from a (Zn,Mn)(S,Se) epilayer containing a 8 nm (Zn,Cd)Se QW. Note the differing rates of band gap closure with increasing temperature..